CCCXXII.—*Dynamic Isomerism involving Mobile Hydrocarbon Radicals. Part II. The Intramolecular Character of the Amidine Rearrangement.*

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IN Part I of this series (J., 1929, 2133) it was shown that when the two isomeric diphenyl-*p*-tolylbenzenylamidines (I) and (II) were

$$\text{(I.)}\quad \mathrm{NPh{:}CPh{\cdot}NPh(C_7H_7)} \qquad \mathrm{NPh_2{\cdot}CPh{:}N(C_7H_7)}\quad \text{(II.)}$$

heated at a sufficiently high temperature they underwent mutual interconversion by migration of a phenyl group from one nitrogen atom to the other, similar equilibrium mixtures of the two isomerides being obtained from both compounds.

This rearrangement bore a close resemblance, both in form and in conditions, to the conversion of imino-aryl ethers into the corresponding amides, *e.g.*,

$$\mathrm{OPh{\cdot}CPh{:}NPh} \xrightarrow{\text{heat}} \mathrm{O{:}CPh{\cdot}NPh_2}$$

which had previously been shown to be intramolecular (J., 1925, **127**, 1992) for the following reasons : (*a*) The change occurred completely without the formation of by-products, (*b*) the progress of the rearrangement could be represented accurately by the formula for a unimolecular reaction, and (*c*) no interchange of groups took place between the molecules of two different imino-ethers when heated together to give a mixture of the corresponding amides.

Similar tests applied to the amidine change were complicated by the reversibility of this rearrangement and by the fact that the compounds were not completely stable. Exposure to the higher temperature required for conversion always caused some darkening and decomposition, although this could be minimised by repeated purification of the material used.

The conversion of the members of a pair of isomeric amidines into an equilibrium mixture was found to follow a unimolecular course as represented by the formula for a reversible reaction. An example is given in the following table, the data being taken from those of Part III (following paper). (Time is expressed in minutes, and logarithms to the base 10 are employed.)

Interconversion of $\mathrm{NPh{:}CPh{\cdot}NPh{\cdot}C_6H_4Cl}(p)$ (I*c*) *and* $\mathrm{NPh_2{\cdot}CPh{:}N{\cdot}C_6H_4Cl}$ (*p*) (II*c*) *at* 330—331° (*corr.*).

Time (mins.)	20	40	60	90	120	
Change, %, I*c* ⟶ II*c* (i)	8	13	19	25·5	30	
Change, %, II*c* ⟶ I*c* (ii)	13	20	26·5	36	38·5	
Total change [(i) + (ii)] (iii) ...	21	33	45·5	61·5	68·5	
Equilibrium, %, I*c*	61·5	61	58·5	58·5	56·5	Mean 59
*$(k + k') \times 10^3$, calc. from (i)	4·65	4·2	4·55	4·7	4·75	
*$(k + k') \times 10^3$, calc. from (ii)	5·35	4·5	4·35	4·55	3·85	
$(k + k') \times 10^3$, calc. from (iii)	5·2	4·3	4·4	4·6	4·25	Mean 4·5

* The mean equilibrium position is assumed in calculating these values.

Repeated recrystallisation of *N*-diphenyl-*N'*-*p*-tolylbenzenylamidine (II) with change of solvent did not alter its rate of conversion into its isomeride (I), nor was the velocity of change affected by the use of a silica in place of a glass vessel. There was therefore no obvious indication that the progress of the reaction depended on the presence of a catalyst.

In those triarylbenzenylamidines (such as III and IV) where all three aryl groups attached to the nitrogen atoms are the same, migration of a group from one nitrogen atom to the other presumably

$$\text{(III.) } NPh{:}CPh{\cdot}NPh_2 \qquad N(C_7H_7){:}CPh{\cdot}N(C_7H_7)_2 \text{ (IV.)}$$

takes place under conditions similar to those required for the unsymmetrical compounds, but as the product of the migration is identical with the original material no change can be observed. The stability of such compounds under the conditions required for rearrangement provides a measure of the extent to which by-product formation takes place. It was found that after carefully purified *triphenylbenzenylamidine* (III) had been heated at 345° for 2 hours, a time almost sufficient to bring the isomerides (I) and (II) into equilibrium, its m. p. had been depressed by only 2°. *Tri*-p-*tolylbenzenylamidine* (IV) was also fairly stable, its m. p. being depressed 2° after 1 hour's heating at 335°. The formation of by-products, even at these high temperatures, was therefore only slight.

To determine whether interchange of groups occurred during rearrangement, a mixture of compounds (III) and (IV) was made in such proportion as to yield on hydrolysis the eutectic mixture of diphenylamine and di-*p*-tolylamine. This was analysed before and after being heated at 330—331° for ½ and for 1 hour. Exposure at this temperature for 1 hour was more than would be necessary for half conversion of (I) and (II) into their equilibrium mixture, and if any exchange of groups had taken place between molecules of (III) and (IV), new amidines yielding phenyl-*p*-tolylamine on hydrolysis would have been formed in appreciable amounts. The melting points of the mixtures of secondary amines obtained from the material before and after heating differed, however, by less than 1·5°, which was within the limits of error of the experiment.

It must, therefore, be concluded that the reversible rearrangement of the triarylamidines is, like the conversion of the imino-aryl ethers into the corresponding amides, an intramolecular process.

EXPERIMENTAL.

Velocity of Rearrangement of Compound (II) *after Successive Crystallisations*.—A specimen of *N*-diphenyl-*N'*-*p*-tolylbenzenylamidine (II) after two crystallisations from a mixture of equal parts of acetone and alcohol (A) was successively recrystallised from a similar mixture of the redistilled solvents (B) and from redistilled light petroleum (C). Samples (5 g. each) of these products were heated in test-tubes simultaneously in an oil-bath at 330—331° (corr.) for 1 hour, and the melts were analysed by the method described in Part I, with the following results :

Specimen	A	A	B	C	C (silica tube)
M. p. of mixture of secondary amines	56·2°	55·6°	56·5°	57·3°	55·4°
Per cent. of (I) formed	41	40	40·5	42	40

The variations are not related to the degree of purification and are within the limits of experimental error.

The new amidines were prepared from the corresponding anilideiminochlorides and secondary amines in the manner described in Part I.

Triphenylbenzenylamidine (III) crystallised from a mixture of equal volumes of acetone and alcohol in tiny yellow needles, m. p. 168—169° (Found: N, 8·2. $C_{25}H_{20}N_2$ requires N, 8·05%). Diphenylamine (m. p. 54—55°) and aniline (identified as acetanilide, m. p. 114—114·5°) were obtained on hydrolysis.

Tri-p-*tolylbenzenylamidine* (IV) crystallised from the same solvent in long lemon-yellow needles, m. p. 188—189° (Found: N, 7·2. $C_{28}H_{26}N_2$ requires N, 7·2%), and yielded *p*-toluidine (m. p. 42·5—43·5°) and di-*p*-tolylamine (m. p. 78—80°) on hydrolysis. Both amidines were very sparingly soluble in alcohol but readily soluble in acetone.

Melting Points of Mixtures of Diphenylamine and Di-p-*tolylamine.*—

$NHPh_2$ (% by wt.)	0	10·9	19·5	30·2	39·4	50·1
$NHPh_2$ (mols. %)	0	12·5	22·0	33·6	43·1	53·9
M. p.	80·3°	74·3°	69·5°	62·5°	56·4°	47·8°
$NHPh_2$ (% by wt.)	58·3	67·7	79·6	87·6	100	
$NHPh_2$ (mols. %)	61·9	71·0	82·0	89·2	100	
M. p.	41·0°	39·8°	45·5°	49·5°	55·5°	

Heating of a Mixture of Triphenyl- and Tri-p-*tolyl-benzenylamidines.*—A mixture of the two amidines containing approximately 66% of the triphenyl compound was made by fusing the two components together, and two samples (5 g. each) were heated for ½ and for 1 hour respectively at 330—331° (corr.). The m. p.'s of the secondary amine mixtures obtained on hydrolysis were as follows:

Time of heating (mins.)	0	0	30	60
M. p. of mixture	36·7°	36·1°	36·2°	35°

Tri-p-*chlorophenylbenzenylamidine*, prepared from di-*p*-chlorodiphenylamine and benz-*p*-chloroanilideiminochloride, formed yellow crystals, m. p. 147—148°, from acetone–alcohol (Found: Cl, 23·6. $C_{25}H_{17}N_2Cl_3$ requires Cl, 23·6%), but was not sufficiently stable above 300° to be employed for the experiments of this series. On hydrolysis it yielded *p*-chloroaniline (m. p. 71°) and di-*p*-chlorodiphenylamine (m. p. 78—79°).

Di-*p*-chlorodiphenylamine is conveniently prepared by direct chlorination of benzoyldiphenylamine in chloroform solution, followed by hydrolysis of the resulting benzoyldi-*p*-chlorodiphenylamine with boiling alcoholic potash. The preparation was described by Claus and Schaare (*Ber.*, 1882, **15**, 1286; compare J., 1929, 569), but the constitution of the product was not determined. This has now been established by independent synthesis through N-p-*chlorophenylbenzimino*-p-*chlorophenyl ether* (stout, pale yellow needles, m. p. 68—69°. Found: Cl, 20·6. $C_{19}H_{13}ONCl_2$ requires Cl, 20·75%) and by direct comparison of the benzoyl derivative and free amine with those obtained by the chlorination of benzoyldiphenylamine. The identities of these compounds and of those obtained by hydrolysis of the various amidines were all confirmed by the method of mixed melting points.

Di-*p*-chlorodiphenylamine had m. p. 78—79°, constant on repeated recrystallisation from light petroleum (Claus and Schaare give m. p. 80°; Burton and Gibson, J., 1926, 2246, give m. p. 71—72°).

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